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Spatial Distribution and Sources Identification of Polycyclic Aromatic Hydrocarbons in Wolong Lake, Northeast China

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Abstract: The aquatic ecosystem maybe significantly affected by polycyclic aromatic hydrocarbons (PAHs) released from fresh water sediments. In order to protect biodiversity, the spatial distribution and sources of PAHs in the sediment of Wolong Lake in Northeast China were studied. A total of 17 surface sediment samples were collected and 12 PAHs were analyzed. The results were as follows. The concentration of total PAHs (TPAHs) ranged between 1412.9 μg/kg and 3948.3 μg/kg (dry weight). Indeno [1, 2, 3-c, d] pyrene was the dominant contaminant which accounted for 87%–98% of TPAHs. Diagnostic ratios of PAHs and principal component analysis showed that biomass combustion and vehicle emissions were likely to be the dominant sources of PAHs in the sediment. PAHs can be considered safe in the context of environmental and human health protection, based on the overall toxicity. Individual PAHs were positively correlated with total organic carbons. These results will be helpful to control PAHs and protect the aquatic ecosystem in the lake.

Keywords: polycyclic aromatic hydrocarbons (PAHs); Wolong Lake; lake sediment; contaminant oxicity; spatial distribution

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous organic contaminants released from the activities associated with combustion and petroleum production. Sixteen PAHs have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their potential as carcinogens and mutagens, as well as environmental persistence (Yunker *et al.*, 2002). Due to their hydrophobic nature, PAHs can be adsorbed easily on particulate matter and accumulated in soil/sediments. As a result, these pollutants expose benthic biota to toxicants with potential food-chain effects (Tamamura *et al.*, 2009; Wang *et al.*, 2013). Consequently, the PAH levels in sediments can provide valuable pollution information and indicate environmental risks (Kuwae *et al.*, 2013).

The Wolong Lake once was called Xipaozi, and has existed since the late Mesozoic Cretaceous Era, with a three million year history. It is approximately 60 km^2 in size, located in the north of Liaoning Province, China. The lake is categorized as a Level 1 ecological sensitive zone in China. The annual mean precipitation is 537.7 mm (70%–80% of the total from June through September). Wolong Lake is the largest natural inland wetland in Liaoning Province, serving as an ecologically

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important body of water. For example, the lake functions inclimate adjusting in the north of Liaoning Province. It also prevents the expansion of the Horqin Sandy Land, maintaining the ecological balance in this area. There are unique habitats for various animals of which more than 828 species have been identified. The rivers of East Malian, West Malian, Erdao, and Channel 541 are the main input rivers of the lake. In 2001, Wolong Lake was designated 'the Provincial Nature Reserve of the Wolong Lake in Shenyang' in order to protect the wetlands and its diverse ecosystem. Agence Française de Développement (AFD) financed Wolong Lake biodiversity conservation and wetland protection project in 2013 (http://www.ambafrance-cn.org/Restauration-des-zones-humides-de-Liaoning).

Wolong Lake is sensitive to environmental change and is important for the protection of the ecosystem in this area. However, water and sediment quality have rarely been investigated. Thus, the aims of this study were to: 1) survey the PAHs in the lake sediment; 2) identify the sources and distribution of PAHs; 3) assess potential risk of PAHs in order to protect the biodiversity of the lake.

2 Materials and Methods

2.1 Sediment sampling

A total of 17 surface sediment samples were collected from Wolong Lake in the dry season (May) in 2014. Locations of the sampling sites are shown in Fig. 1. All surface sediment samples (0–20 cm) were collected with a Peterson sampler and homogenized on site. The samples were then immediately stored in glass bottles with Teflon-lined capsat −20℃ until further treatment.

2.2 PAHs extraction and analysis

The stored sediment samples were homogenized andfreeze-dried. Extraction of PAHs was performed according to current procedures (Li *et al*., 2008). About 3 g of dried sediment samples were placed in 50 mL Teflon centrifuge tubes, and 20 mL of dichloromethane was added to each tube. The sediment was then extracted using an ultrasonic extractor for 2 h. After extraction, the sediment slurry was centrifuged at 4000 rpm for 10 min. A total of 10 mL of supernatant was dried by evaporation of dichloromethane under a stream of nitrogen and then dissolved in 2 mL acetonitrile and filtered through a 0.22 μm organic filter. The moisture content of the freeze-dried sediments was determined at 105℃ for 8 h to allow all the data to be presented on the dry matter.

The concentrations and profiles of PAHs in 2 mL of acetonitrile were analyzed by high-performance liquid chromatography (HPLC series 1200s Agilent) fitted with a ZORBAX Eclipse XDB-C18 column (5 μm, 250 mm × 4.6 mm). Elution conditions were as follows: a 2:3 (v/v) mixture of water and acetonitrile was used as the solvent at a flow rate of 0.5 mL/min throughout. All

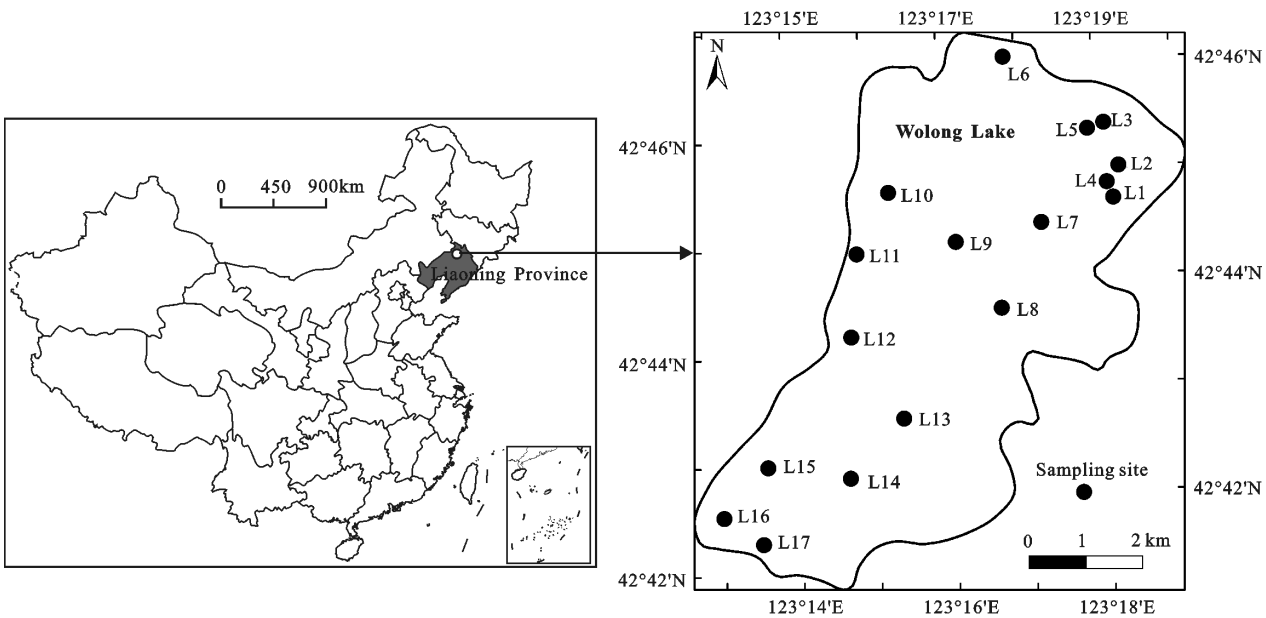

Fig. 1 Location sketch of sampling sites in Wolong Lake, Liaoning Province, China

the processes lasted 55 min, and 10 μL of sample was injected into the HPLC by the autosampler. Identification and quantification of 16 PAH compounds were based on matching their retention time.

The following 12 compounds were detected in this study: acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), ben-zo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1, 2, 3-c, d]pyrene (IcdP), and benzo[g, h, i]perylene (BghiP).

2.3 Quality assurance and quality control

An internal calibration procedure with a mixture of PAH standards was used to quantify PAH concentrations. The correlation coefficients for the five concentration gradients ranged from 0.995 to 0.999. A calibration standard was analyzed to determine the accuracy of the calibration curves and to estimate the repeatability and accuracy of the analytical method during the analysis process. The recovery of PAHs was assessed by spiking clean sediments at known concentrations. The recovery of PAHs was between 80%–110%.

2.4 Data analysis

The positions of sample locations were recorded using a GPS receiver (e Trex Venture, USA). The WGS84 coordination system from the GPS receiver was transformed to the TM coordination system to fit the actual map. For the distribution map, software ArcGIS10.3 Copyright 1999-2013 Esri was used (ArcGIS10.3 Copyright 1999-2013 Esri).

3 Results and Discussion

3.1 PAHs concentrations in sediments

The concentrations of 12 measured total PAHs (TPAHs) in lake sediments ranged from 1412.9 μg/kg to 3948.3 μg/kg (dry weight, dw), with a mean of 2251.9 ± 649.0 μg/kg (Table 1). The dominant component of TPAHs was 6-ring PAHs (IcdP), with 92.6% of TPAHs, followed by 3-ring, 4-ring and 5-ring PAHs. However, Flua and BghiP were undetected. The total potentially carcinogenic PAHs (TcPAHs), including BaA, Chr, BbF, BkF, BaP, IcdP ranged from 1377.1 μg/kg to 3571.2 μg/kg dw with an average concentration of 2147.0 μg/kg dw. The composition of TcPAHs consisted of 97% IcdP, 0.81% BaA, 0.75% BbF, 0.55% BaP, 0.47% Chr and 0.38% BkF.

Direct comparison of data in the literature regarding PAHs was somewhat difficult due to differences in the analytical methods, representative samples, annual seasons, and detected PAH components. Nevertheless, a comparison of the sestudies may provide insight into the

Table 1 Concentrations and profiles of 12 USEPA-PAHs in sediments of Wolong Lake

PAHs	Minimum (μg/kg dw)	Maximum (μg/kg dw)	Mean (μg/kg dw)	Standard deviation	Variance coefficient
Flu+Ace	0.0	73.6	36.6	18.8	0.5
Phe	0.0	216.7	40.9	56.4	1.4
BaA	0.0	27.6	16.3	7.1	0.4
Chr	5.5	27.4	10.1	5.8	0.6
Flua	–	–	–	–	–
Pyr	5.5	87.0	27.5	19.5	0.7
BaP	0.0	28.5	11.1	6.0	0.5
BbF	6.7	52.2	16.2	11.3	0.7
BkF	0.0	22.3	7.3	4.7	0.6
BghiP	–	–	–	–	–
IcdP	1311.5	3452.6	2086.0	583.0	0.3
3-ring	6.3	290.1	77.4	72.8	0.9
4-ring	11.2	119.8	53.8	27.2	0.5
5-ring	12.1	85.8	34.6	16.2	0.5
6-ring	1311.5	3452.6	2086.0	583.0	0.3
TPAHs	1412.9	3948.3	2251.9	649.0	0.3

Notes: '–' means that PAHs were undetected. USEPA-PAHs means the United States Environmental Protection Agency-polycyclic aromatic hydrocarbons

changing levels of PAHs in China and around the world (Table 2). PAH concentrations reported in the present study were significantly higher than those reported in the lakes in Northeast China and lower than those in lakes of Taihu (China), Nansi (China), Victoria (Kenya), Maryut (Egypt) and Naples harbor (Italy). The concentration of PAHs was high primarily due to the IcdP concentration in Wolong Lake. In general, PAH compounds with three and four aromatic rings (i.e. Phe, Flua, Pyr) were dominant in the gaseous phase, while higher molecular weight PAHs (i.e., BaP, IcdP, BghiP) were more likely to remain in the particulate phase (Liu *et al*., 2013). Based on the following results in the present study, the pathway of PAHs entering into the lake was largely from runoff and air deposition (not from Kangping County). Hence, the higher molecular weight PAHs

Table 2 Comparison of concentrations of total polycyclic aromatic hydrocarbons (TPAHs) in lake sediment

Country	Lake	*N*	TPAHs (μg/kg)			Reference
			Min	Max	Mean	
China	Dianchi	16	210	11070	1543	Zhao *et al*., 2014
	Taihu (Sep.)	29	255	1059	581	Tian *et al*., 2014
	Taihu (May)	29	209	1003	472	
	Taihu	25	1207	4754	2563	Qiao *et al*., 2006
		28	180	1669	533	Lei *et al*., 2014
		35	410	5260	1440	Qu *et al*., 2002
	Chaohu	35	61	10200	1230	Wang *et al*., 2011
		15	101	6245	733	Qin *et al*., 2014
		15	81	30365	2235	Li *et al*., 2014
	Baiyangdian	16	101	323	190	Hu *et al*., 2010
	Nansi	16	160	32600	6143	Li *et al*., 2009
	Poyang	16	33	369	157	Lu *et al*., 2012
	East Lake	126	10.9	2478.1	685.8	Yun *et al*., 2016
	Hongfeng	1	2936.1	5282.3		Guo *et al*., 2011
	Qinghai	14	366	966		Wu *et al*., 2014
	Wanghua	1	140	363	223	
	Lianhuan	1	293	2247	767	Sun *et al*., 2014
	Keqin	1	215	1308	694	
	Mopanshan		187.3	453.2	320.2	Liu *et al*., 2013
	Dahuofang	24	323	912	592	Lin *et al*., 2013
	Maar	1	474	2289	1496	Guan *et al*., 2012
	Wolong	17	1412.9	3948.3	2251.9	Present study
Italy	Naples harbor	189	9	31774	3142	Sprovieri *et al*., 2007
Turkey	Iznik	12	17	835	200	Ünlü *et al*., 2010
USA	Nicaragua	20	10	640		Scheibye *et al*., 2014
	Michigan	24	213	1291	567	Huang *et al*., 2014
	Erie	16	224	5304	2088	Smirnov *et al*., 1998
Philippines	Laguna	5	110	170	136	Hallare *et al*., 2005
Kenya	Victoria	2	15560	66790	41175	Kwach *et al*., 2009)
Japan	Biwa	19	599	1660	1186	Itoh *et al*., 2010
Malaysia	Chini	39	248	8098		Bakhtiari *et al*., 2009
India	Nainital	10	12000	216000		Choudhary *et al*., 2010
	Bhimtal	5	1000	217000		
Russia	Baikal	15	220	1256	452	Ok *et al*., 2013
Estonia	Pihkva	1	75	345		Kapanen *et al*., 2013
Egypt	Manzala	11	131	1740	361	Barakat *et al*., 2013
	Maryut	39	106	57800	6950	Barakat *et al*., 2011

Notes: *N* is number of samples

were easily accumulated in the lake, resulting in the higher concentrations observed. However, the precise explanation for the high incidence of IcdP needs further study.

3.2 Distribution of PAHs

Fig. 2 shows the spatial distribution of TPAHs in the dry season in Wolong Lake. In the dry season, the concentration of TPAHs decreased gradually from southwest to northeast, with low concentrations of TPAHs near the boundary of the northeast. The spatial distribution of PAHs was similar to that from Tamamura *et al*. (2009), although contrary to the results of Tian *et al*. (2014) and Kwach *et al*. (2009).

The different spatial distribution of PAHs might generally be attributed to: 1) Seasonal effects, for example, in the wet season (June–September) PAHs were predominantly originating from street surface runoff, industrial discharges, and runoff from rural deposition of transported residues in combustion, while in the dry seasons, PAHs were mainly derived from the deposition of air particles (Zhao *et al*., 2014). 2) The biodegradation of the PAHs, for instance, after entering the aquatic environment, PAHs can have various fates, including biological uptake, microbial degradation, volatilization, photo oxidation, and sedimentation (Cui *et al*., 2011). 3) The varying composition of particle sizes at different sample sites affects the concentrations of PAHs. For instance, it was notable that the sediments closer to the shore were coarser and silt-sized in contrast to sediments more inshore which were finer in texture. Coarser sediments supported higher rates of biodegradation than fine sediments (Yunker *et al*., 1996). 4) The internal processes of the lake ecosystem. For example, Hsu *et al*. (2007) found that sediment contamination was relatively constant in the Dommel River with stable hydrological conditions, while a decrease in sediment toxicity was observed in spring caused by high water discharge and algal blooms in the Elbe River. In Wolong Lake, differing sources and biodegradation were likely the primary reasons for the different spatial distribution of the PAHs observed. The high concentration in southwest of Wolong Lake might have resulted from two possible conditions: 1) the upstream West Malian River, the main inlet river in the southwest of Wolong Lake, is situated in the coal mining town of Zhangqiang. Accumulations of coal piled in this area might release PAHs that drained into the lake. 2) The area 32 km^2 to the southwest of the lake was once farmed as rice land before 2008. As a result, the combustion of oil used for agricultural machinery may have increased PAHs draining into the lake.

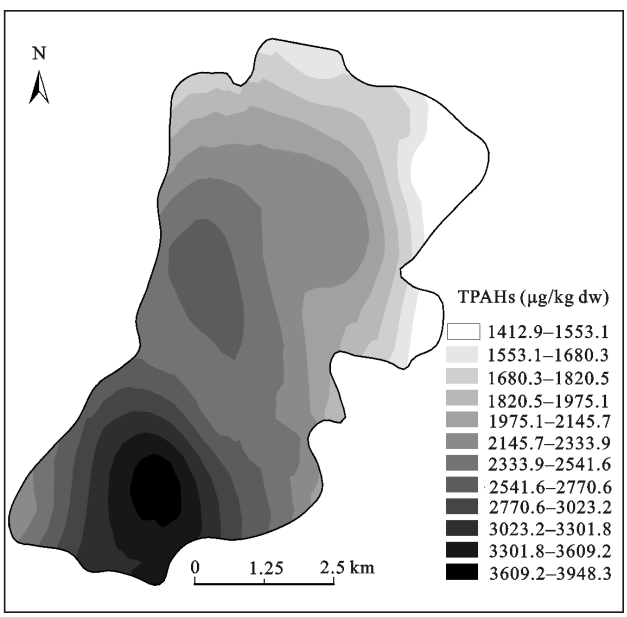

Fig. 2 Spatial distribution of total polycyclic aromatic hydrocarbons (TPAHs) in Wolong Lake

The concentration of PAHs in the northeast of Wolong Lake, which was close to Kangping City, was lower than those in other sites. The primary reasons might be attributed to dominant wind in this area. Northerly winds prevail in winter and summer, while northerly winds and southwest winds are predominant in spring and autumn (Zou *et al*., 2014). Under these conditions, the PAHs in the air originating in the city would have little chance to be deposited in the lake, resulting in the low concentrations observed.

3.3 Possible sources of PAHs in surface sediments

The concentration ratios of specific PAHs and principal component analysis (PCA) were used to present the sources of PAHs in sediment in the present study (Simcik *et al*., 1999). In this study, ∑LPAHs/∑HPAHs ratios were < 1 (the PAHs of low/high molecular weight (LPAHs/HPAHs)), indicating they were likely to have originated from pyrogenic sources (Chen and Chen, 2011). BaA/(BaA + Chr) ratios > 0.35 imply combustion (Yunker *et al*., 2002). Fig. 3 presented a PAH cross-plot for these ratios for all sediments analyzed in Wolong Lake. Based on above ratios, most of the PAHs in sediments were due to combustion sources.

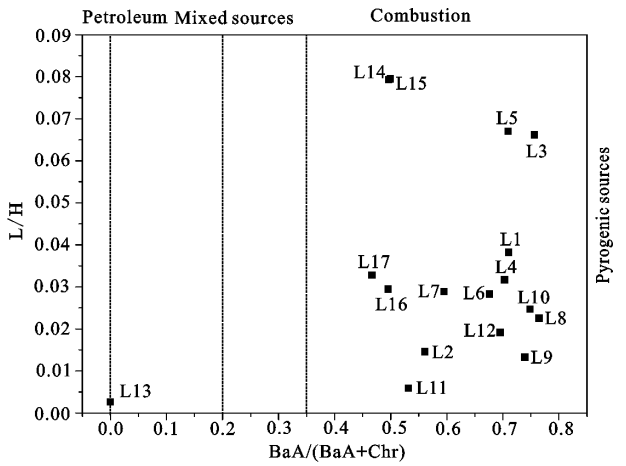

Fig. 3 Polycyclic aromatic hydrocarbons (PAHs) cross plot in sediments of Wolong Lake. L, low high molecular weight PAHs (2- and 3-ring); H, high molecular weight PAHs (4- and 6-ring); BaA, benzo[a]anthracene; Chr, chrysene

Based on previous studies, Phe, Pyr and BaA had been generally attributed to biomass combustion (grass, wood, and coal combustion) (Zuo *et al*., 2007). BbF and BkF were proposed as indicators of diesel-powered vehicle exhaust (Robinson *et al*., 2006). BaP was reported to originate from vehicle emissions such as gasoline (Larsen and Baker, 2003). IcdP has been found both in the combustion systems of gasoline engines and in diesel-powered vehicle emissions (Zhang *et al*., 2011; Wang *et al*., 2012).

PCA revealed three principal components with eigenvalues > 1.0, accounting for 86% of the total variance. Table 3 shows the rotated factors of normalized PAHs. Factor 1 (PC1) was highly loaded on Phe, Pyr, BbF, and BkF, accounting for 45% of the total variance, meaning that the primary sources of PAHs were the combination of biomass combustion and vehicle emission. PC2, predominately composed of BaA, was responsible for 25.5% of the total variance, which implied the second contributing sources were biomass combustion in Wolong Lake. PC3 was heavily weighted towards BaP indicating gasoline from vehicle emission, at 15.3% of the total variance.

In Northeast China, biomass (grass, wood, or coal) was still the main material burned for household heating in winter and for cooking in rural areas. However, there has been a recent switch to cooking with gas since 2000 (Sun *et al*., 2014; Zhao *et al*., 2014). The predominant source of income in the study area was dependent on the production of fruits and vegetables; therefore, vehicle emissions (gasoline or diesel combustion) as a result of food transportation were likely to have contributed to the concentration of PAHs.

Table 3 Loading of polycyclic aromatic hydrocarbons after varimax rotation

PAHs	PC1	PC2	PC3
Flu+Ace	0.58	0.74	–0.07
Phe	0.89	0.37	–0.17
BaA	–0.01	0.92	0.16
Chr	0.44	0.61	–0.48
Pyr	0.87	0.44	0.09
Bap	0.09	0.11	0.90
BbF	0.87	0.36	0.17
BkF	0.92	–0.20	–0.08
IcdP	0.63	0.10	–0.49
percentage of variance (%)	45.3	25.5	15.3
Cumulative (%)	45.3	70.8	86.1
R^2	0.737		

3.4 Toxicity of PAHs

Toxic equivalency factors (TEFs) of PAHs were used to assess carcinogenic potency in terms of BaP equivalent concentrations, indicating the quantitative potential toxicological significance to human health (CCME, 2010).

The overall toxicity or toxic equivalents (TEQs) of PAHs calculated for sample sites varied from 155.7 ng/g to 366.2 ng/g with an average of 223.9 ng/g (Table 4). In the sediments tested, IcdP (average 92.7%, range 84.2%–98.7%) contributed the highest carcinogenic exposure equivalent, and was considered to be the most hazardous, followed by BaP (average 5.7%, range 0–13.2%). Sites with the highest toxicity were L14 (366.2 ng/g) in the southwest area of the lake. The spatial distribution difference of toxicity might indicate different sources, which were largely from biomass combustion in L14, based on the PCA results. The average TEQs in the current study were significantly lower than those obtained from sediments in the lakes presented in Table 4, except the Nansi Lake and Lake Manzala. Based on the PAH carcinogenic effects, safe TEQs of PAHs should be < 600 ng/g (Li *et al*., 2014). Therefore, the PAHs in Wolong Lake are likely to be safe for the protection of environmental and human health.

The effect range-low (ERL) and effect range-median

Table 4 Toxic equivalents (TEQs) of polycyclic aromatic hydrocarbons (PAHs) in sediments of lakes and harbors

Country	Lake	*N*	Min (ng/g)	Max (ng/g)	Mean (ng/g)	Std	
China	Kaohsiung Harbor	12	55.0	1964.0	750.5	830.7	Chen and Chen, 2011
	Dianchi	23	19.0	967.0	154.0	188.1	Zhao *et al*., 2014
	Nansi	5	0.2	202.2	45.2	87.9	Li *et al*., 2009
	Taihu	25	94.0	856.0	407.0		Qiao *et al*., 2006
	Chaohu	12	40.7	614.0	344.0		Li *et al*., 2014
Egypt	Manzala	11	19.9	242.2	54.1		El-Sayed *et al*., 2013
Italy	Naples harbor	189	2.0	4723.0	428.0	368.9	Sprovieri *et al*., 2007
	Naples harbor	160	1.0	4911.0	362.0	522.0	Feo *et al*., 2011
China	Wolong	17	155.7	366.2	223.9	58.3	Present study

Notes: *N* is number of samples

(ERM) have been developed to quantitatively assess the adverse biological effects in sediments (Long *et al*., 1995). TPAHs were below the ERL for all the sites. This finding was unlike that found in Australia and in the USA where sediment guidelines have been developed according to toxicity of benthic biota. These data were subject to the Interim Sediment Quality Guidelines (ANZECC and ARMCANZ, 2000) and the Consensus Based Sediment Quality Guidelines by MacDonald *et al*. (2000) to help water managers assess local waterbodies. However, China does not currently have such guidelines. Nonetheless, there has been recent work toward the development of local indicator species, thus enabling China to begin the process of developing guidelines for local aquatic systems.

3.5 Relationship between TOC and PAHs

TOC (total organic carbon) was an important factor in contributing to the distribution of PAHs in sediment, and the positive correlation between concentrations of PAHs and TOC has been reported in many studies (Viguri *et al*., 2002). The positive correlation indicated that organic matter plays an important role in the retention of PAHs (Shi *et al*., 2007). Another possible interpretation of these results was that the TOC and PAHs areco-emitted with waste waters that originate from non-point sources in the catchment (Liu *et al*., 2013). TOC ranged from 4.0% to 39.1% with a mean of 10.3% in Wolong Lake. The relationship between PAHs and TOC is shown in Table 5.

In Wolong Lake, TOC had significant positive correlation with BkF, BbF, Phe, Pyr and Flu + Ace. Meanwhile, there were positive correlations between TOC and 3-ring, 5-ring or total PAHs. This result was similar

Table 5 Relationship between polycyclic aromatic hydrocarbons (PAHs) and TOC (total organic carbon) in sediments of Wolong Lake

PAHs	Correlation	PAHs	Correlation
Flu+Ace	0.592*	BkF	0.926**
Phe	0.708**	BghiP	–
BaA	–	IcdP	–
Chr	–	3-ring	0.647**
Flua	–	4-ring	–
Pyr	0.657**	5-ring	0.705**
Bap	–	6-ring	–
BbF	0.848**	Total PAHs	0.557*

Notes: *, correlation is significant at the 0.05 level (2-tailed); **, correlation is significant at the 0.01 level (2-tailed); –, correlation is not significant

to the results from other studies, which have found that there was a positive exponential relationship between PAHs and TOC (Viguri *et al*., 2002; Qin *et al*., 2014).

Some studies have reported that the concentration of PAHs was not always correlated with TOC, and the linear regression correlation coefficient between total PAH concentrations (TPAHs) and black carbon (BC) was larger than that between TPAHs and TOC (Bogdal *et al*., 2011; Liu *et al*., 2011). Similarly, the relationship between TOC and PAHs could be affected by many factors, such as the sampling time, the source of TOC, and the molecular weights of PAHs. In lake sediments, it is not unusual for algae-derived organic carbon to have an influence on the distribution of low molecular weight PAHs, more so than that of high molecular weight PAHs (Wu *et al*., 2012). The results from Zhao *et al*. (2014) showed that TOC had a significant positive correlation with 2-ring PAHs, 3-ring PAHs and LPAHs, but no significant correlations with other PAHs and TPAHs in

Dianchi Lake. These data indicate that TOC was primarily derived from the aquatic plants and algae. In this present study, individual PAHs were correlated with TOC and both 3-ring and 5-ring PAHs correlated with TOC. A similar difference was also reported by Feng *et al.* (2007), which showed that the relationship between total PAHs and TOC was not significant although some individual PAH concentrations correlated well with TOC content.

4 Conclusions

As the key component of a frail ecological environment in Northeast China, Wolong Lake has been contaminated by PAHs. The TPAHs in the sediments was shown to be safe for the protection of environmental and human health based on the overall toxicity. The relationship between TOC and PAHs varied with the seasons due to the different sources of TOC. According to the spatial distribution and source identification, combustion might be the dominant source of TPAHs in this lake. West Malian River runoff and air deposition might be the main sources of PAHs entering into the lake. Hence, decreasing the burden from the runoff and air deposition will be helpful to control the concentration of PAHs and protect the aquatic ecosystem in the lake.

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